SELECTIVE RADIATION FROM VARIOUS SOLIDS.

By W. W. Coblentz.

I. INTRODUCTION.

Our knowledge of the emission of radiant energy from various substances at different temperatures is extremely limited, being confined to platinum in the case of metallic electrical conductors, to several gases in vacuum tubes, to water-vapor and carbon dioxide in the Bunsen flame, to carbon, to the oxides of copper and iron, and to the radiation from an uniformly heated cavity or theoretically complete radiator. The emission spectra of the Bunsen flame and of gases in vacuum tubes were found to be composed of sharp emission bands superposed upon a weak continuous spectrum. The solids were found to have smooth continuous emission spectra, and it seems to be the general expectation to find that all solids emit continuous spectra.[1]

To Paschen is due the credit for the first systematic study of the spectral distribution of radiant energy from various solids and from the Bunsen flame. Subsequent work by others has been but little more than the establishment of the co-called radiation constants to a greater number of significant figures than was possible by Paschen, with the facilities at his disposal.

The best experimental proof of Kirchhoff's law of the proportionality of emission and absorption is due to Paschen.[2] He found that the intensity of the emission of the CO_2 band at 4.4μ when using a column of gas 7 cm long was as great as for a column of the gas 33 cm long. In other words, the intensity of the radiation of the column of gas 7 cm long was as great as that of a

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[1] Kayser. Spectroscopie, 2, pp. 135 and 284.
[2] Paschen. Ann. der Phys. (3) 53, p. 26; 1894.

complete radiator for the same wave length and at the same temperature. Unfortunately, the number of radiating substances for which it is possible to determine the temperature, even approximately, is extremely small. Hence the work presented on the following pages can not be more than a qualitative proof of Kirchhoff's law of proportionality between emission and absorption. It has numerous applications, however, particularly in studying substances having sharp emission (and hence sharp absorption) bands. The emission spectra of numerous substances are given here, of which it has not been practicable to study the absorption spectra. Their emission spectra give us some idea of the nature of their absorption, the only difference being that the emission bands are more intense, due to the greater thickness and the higher temperature of the substance examined. Another feature of the results obtained, which is new, is the extreme sharpness of the emission bands. Moreover, the maxima of the emission and absorption bands coincide, although the temperatures at which the two sets of observations were made differ by 500° to 1000° C. The positions of the sharp, well-defined maxima are not affected by change in temperature. This is in marked contrast with the results of Königsberger [3] for the limited region of the visible spectrum, in which he found that for certain selectively absorbing substances the maximum of the absorption band shifts toward the long wave-lengths with rise in temperature, and with the results of Paschen [2] on the emission bands of CO_2 and water vapor, which shifted with rise in temperature, some toward the long, others toward the short wave-lengths. The data may also prove to be useful in determining whether pleochroism is an inter- or intra-molecular phenomenon. For example, the absorption spectrum of Adularia shows a band at 3.2μ, which in the emission spectrum is shifted to 2.9μ. The latter band is characteristic of the silicates, whether in the emission or absorption spectrum. The present work may be considered an examination of the emission spectra of electrical insulators, or so-called "transparent media." The only previous work done on this subject is due to Rubens,[4] who examined the radiation from the Auer mantle,

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[3] Königsberger. Ann. der Phys., **4**, p. 796; 1901.
[4] Rubens. Phys. Zs., **6**, p. 790; 1905.

as well as from mantles composed of the oxides of pure cerium and of pure thorium. The difficulty experienced by him was the elimination of the emission spectrum of the hot gases which was superposed upon that of the oxides composing the mantle. Hence, if he had examined a mantle of zirconium oxide, he would not have been able to detect an emission band which occurs at 4.3μ, since the gas flame has a strong emission band at this point.

The substances used in the present investigation were in the form of solid rods made in an oxy-hydrogen flame, or in the form of thick layers of the substance placed upon a heater. The rods were heated by an electric current from the secondary of a 2000-volt, 300-watt transformer These rods had, of course, to be given an initial heating with an alcohol or blast lamp until they became conducting, just as is necessary with the Nernst glower. A resistance was placed in the primary circuit of the transformer, to regulate the current. The rods were provided with platinum terminals and were securely mounted in incandescent lamp-sockets. After heating them until they became conducting they were securely mounted before the spectrometer slit.

The substances that could not be melted and formed into rods were made into a paste and spread upon the "heater tube" of a Nernst lamp. The "heater tube" consisted of a hollow porcelain tube about 5 cm long and 8 mm diameter, covered with a coil of fine platinum wire, and was used in preference to a platinum strip on account of its rigidity and ease in handling. It gave the same results as the same material on a platinum strip. The spectrometer, the fluorite prism, and the bolometer[4a] were previously used in examining the radiation from the Nernst glower. It is important to notice, however, that by enclosing the optical parts of the instrument it was possible to entirely eliminate the atmospheric absorption bands, which had not been done successfully by previous experimenters. The emission curves are therefore, within experimental errors, an exact portrayal of the distribution

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[4a] In the paper on "Instruments and Methods Used in Radiometry," this Bulletin 4, pp. 420 and 454, the term "*bolometer current*" is accidentally used for "*battery current*," which was 0.04 ampere. The "*bolometer current*" was therefore only 0.02 ampere, but could have been increased to 0.04 ampere, which would have doubled the sensibility.

of the energy emitted in different parts of the spectrum. Unfortunately it is not possible to determine the temperature of the radiating body. A thermocouple can not be applied on account of the loss of heat by conduction. It is of course absurd to attempt to measure the temperature of these substances with an optical pyrometer. For example, the rod of oligoclase was a perfectly transparent glass and emitted no light other than that due to sparking of the platinum terminals. Nevertheless, a substance such as iron oxide at the same temperature would have emitted light, while both emit strongly in the infra-red. Another illustration is the rod of topaz which was an opaque, white mass. On withdrawing it from the oxy-hydrogen flame it was accidentally stroked with an iron forceps, when the parts so stroked emitted a dull red light, due to the greater emissivity of the iron oxide, while the untouched parts retained their usual white color.

Instead of temperatures, the energy consumptions are given; also the dimensions of the rods, the lengths being the distances between the platinum terminals. The diameters are in some cases not very accurate, owing to the irregularity of some of the filaments. The voltage was measured with an electrostatic voltmeter joined to the terminals of the rod. The current was measured with a milliammeter of a suitable range to insure accuracy.

II. RADIATION FROM ELECTRICALLY HEATED SOLIDS.

Prominent among this group of substances are a series of silicates, which have an emission band in common at 2.9μ, characteristic of SiO_2, which is as sharp as any yet found in gases. The absorption spectra of many of these compounds are recorded in a previous paper by the author.[5]

In order to give the reader some idea of the conditions under which the data were obtained, a rough estimation is made of the temperature at which a complete radiator would emit light of a color similar to that given out by the substance under investigation. The length of the rods used depended upon the melting point. The ends of the rods were shielded from the spectrometer slit.

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[5] Carnegie Publication No. 65.—Investigations of Infra-Red Spectra, Carnegie Institution of Washington, Dec., 1906.

Fig. I.
ZIRCONIUM OXIDE
(Zr O₂)
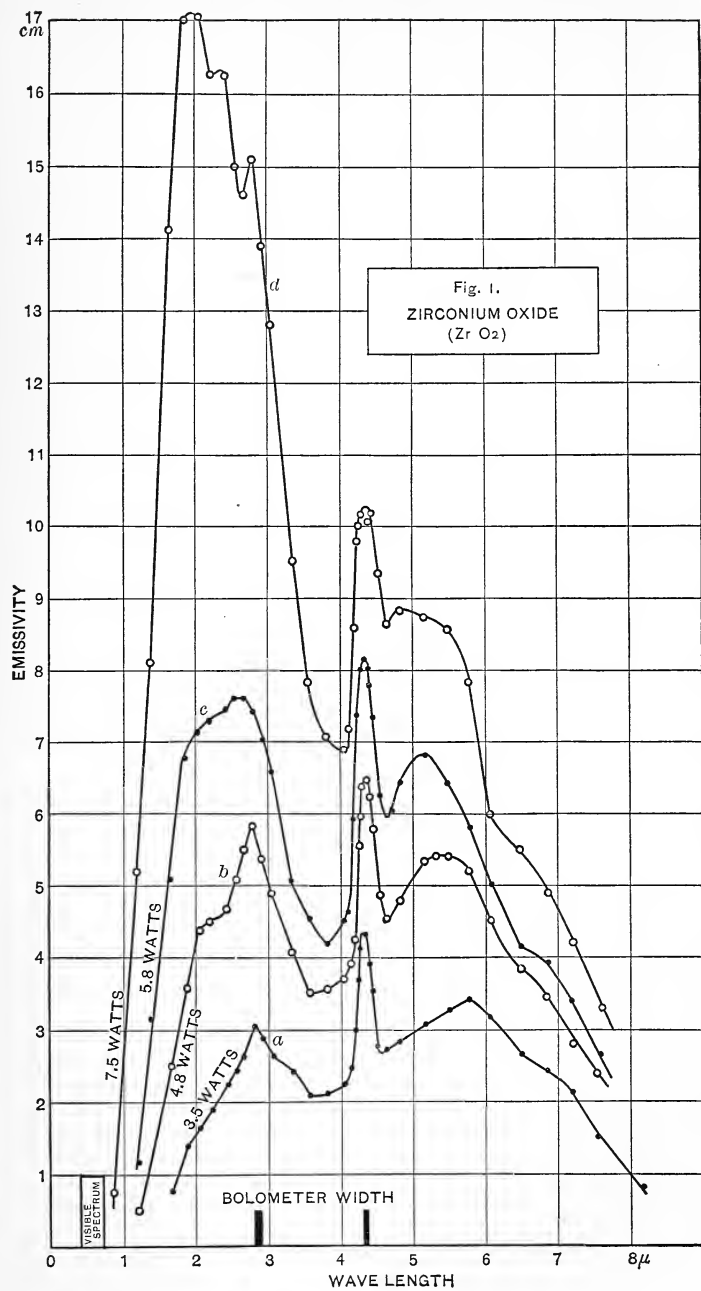
All the curves are reduced to the normal spectrum by dividing the observed galvanometer deflections by the slit-width expressed in wave-lengths. The unsteadiness of the bolometer prevented an accurate mapping of small emission bands occurring beyond 6μ.

1. *Zirconium Oxide* (ZrO_2).—[Rod 10 × 2 × 1.4 mm. Energy consumption, 3.5 (900°), 4.8, 5.6, 8.5 watts. Curves *a, b, c, d*, Fig. 1; and 9.6, 12, and 13.6 (1400°) watts. Curves *a, b, c,* Fig. 2]. The specimen examined was a fragment from a furnace. It probably contained some "binder," although from the curve for the pure material, Fig. 8, it appears that the foreign substance contributed but little to the emission bands. The fine platinum terminals were wound around the ends of the rod, which was about 10 mm long, the distance between the terminals being 5 mm. The curves are conspicuous for their sharp emission band at 4.3μ, which remains superposed upon the continuous background even at a bright yellow heat, corresponding to a temperature of about 1400°. This series of energy curves is one of the best illustrations yet recorded of the gradual shift of the maximum of intensity of emission toward the short wave-lengths, with rise of temperature. For an energy consumption of 3.5 watts the maximum of the envelope of these emission bands lies at 4 to 5μ, and shifts steadily toward the short wave-lengths, being at about 1.8μ for an energy consumption of 13.6 watts. The pure oxide is not an efficient radiator of white light, and only becomes so when a small amount of cerium, thorium, or yttrium oxide is added, which combination is the Nernst glower previously investigated.[6]

In addition to the sharp emission lines at 2.8 and 4.35μ, there are wide hazy bands at 2 and 2.4μ (appears on curve *d*), while from 5 to 6μ there is a wide band which is evidently unresolved, the maximum shifting toward the short wave-lengths with rise in temperature. The extraordinary rapidity which characterizes the growth of the emissivity at 1.5 to 2μ is worthy of notice. In one case where the ratio of emissivities at 4.3μ, for a given increase in energy, is 50, it is almost 200 at 2μ.

2. *Oligoclase*[7] $\left(\dfrac{3\ Na\ Al\ Si_3\ O_8}{Ca\ Al_2\ Si_2\ O_8} \right)$.—[Rod, 9 × 2.8 mm. Energy

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[6] This Bulletin, Vol. 4, p. 533; 1908.
[7] Transmission curves. Carnegie Publication No. 65, p. 64.

Fig. 2.

ZIRCONIUM OXIDE

(Zr O$_2$)
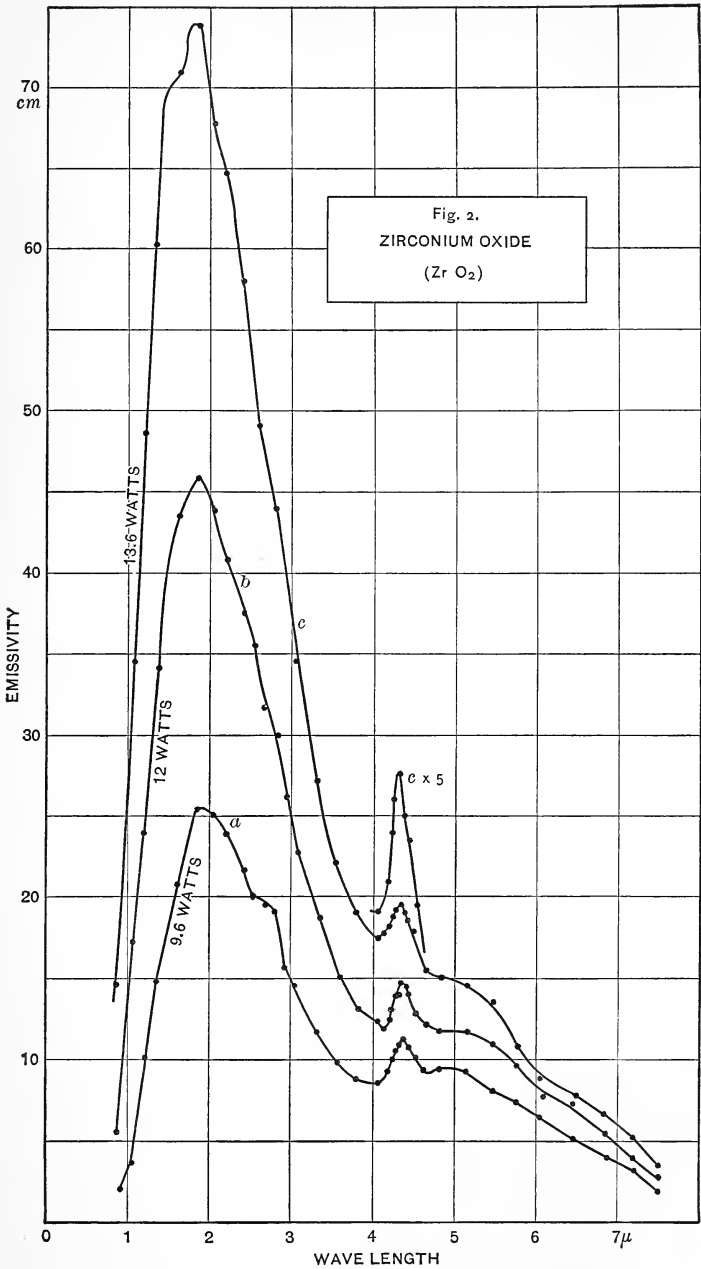
supplied was 8.6 watts and 13.3 watts. Curves a and b, Fig. 3.]
The original crystal, as well as the glass rod, were perfectly trans-
parent. The rod showed no color on suddenly throwing off the
current. The platinum terminals melted on 16 watts, but the rod
showed no color. As in the preceding feldspars there are bands
at 2, 2.88, 3.1, 4.1, 4.5, and 7μ. The absorption band at 4.8μ
seems to be shifted to 4.5μ in the emission spectrum. Curve c
gives the emissivity of a rod 2.5 cm long, 2.1 mm diameter, heated
(on 29.4 watts) until it became viscous (temperature about 1200°
C), but did not sag. The radiation was taken from a length of
5 mm of the central portion of the filament by shielding it. The
curve is conspicuous in showing that at 2μ the intensity has
increased but little as compared with the band at 2.9μ. The
isochromatics of this filament are given in Fig. 14. In curves a
and b the ends of the rod were not shielded, so that some of the
radiation at 1 to 2 may be due to internally reflected radiation of
the hot platinum terminals.

    3. *Albite*[8] ($Na\ Al\ Si_3\ O_8$).—The rod was translucent and seemed
to emit no light except that reflected from the platinum terminals.
The emission band at 2.88μ is more intense than the one found in
orthoclase, as was found in the absorption spectrum. Two other
bands are noticeable at 4.1 and 4.5μ, respectively.

    4. *Orthoclase*[9] (*Var. Adularia*) ($K\ Al\ Si_3\ O_8$).—[Rod, 8 × 2 mm.
Energy supplied, 2.2 and 3.9 watts.] This substance emitted a
little more light than albite, although it was more transparent.
The emission band at 2μ is prominent. The one at 2.9μ is shifted
from its position at 3.2μ in the absorption spectrum, from which
it would appear that the group of atoms causing the absorption
is different in the two cases. An examination of the transmission
spectrum, using polarized light, will be necessary to determine the
true position of the absorption band. The bands at 4.1 and 4.5μ
are in common with the feldspars.

    5. *Beryl* ($Be_3\ Al_2$) ($Si\ O_3)_6$.—[Rod, 10 × 3 mm. Energy, 7 to
8 watts. Curve a, Fig. 4.] The rod was an opalescent, milky
glass, although the original crystal was a transparent green. The

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[8] Transmission curves. Carnegie Publication, No. 65, p. 65.
[9] Transmission curves. Carnegie Publication, No. 65, p. 64.

Fig. 3.
OLIGOCLASE
3:Na Al Si3 O8
Ca Al Si3 O8
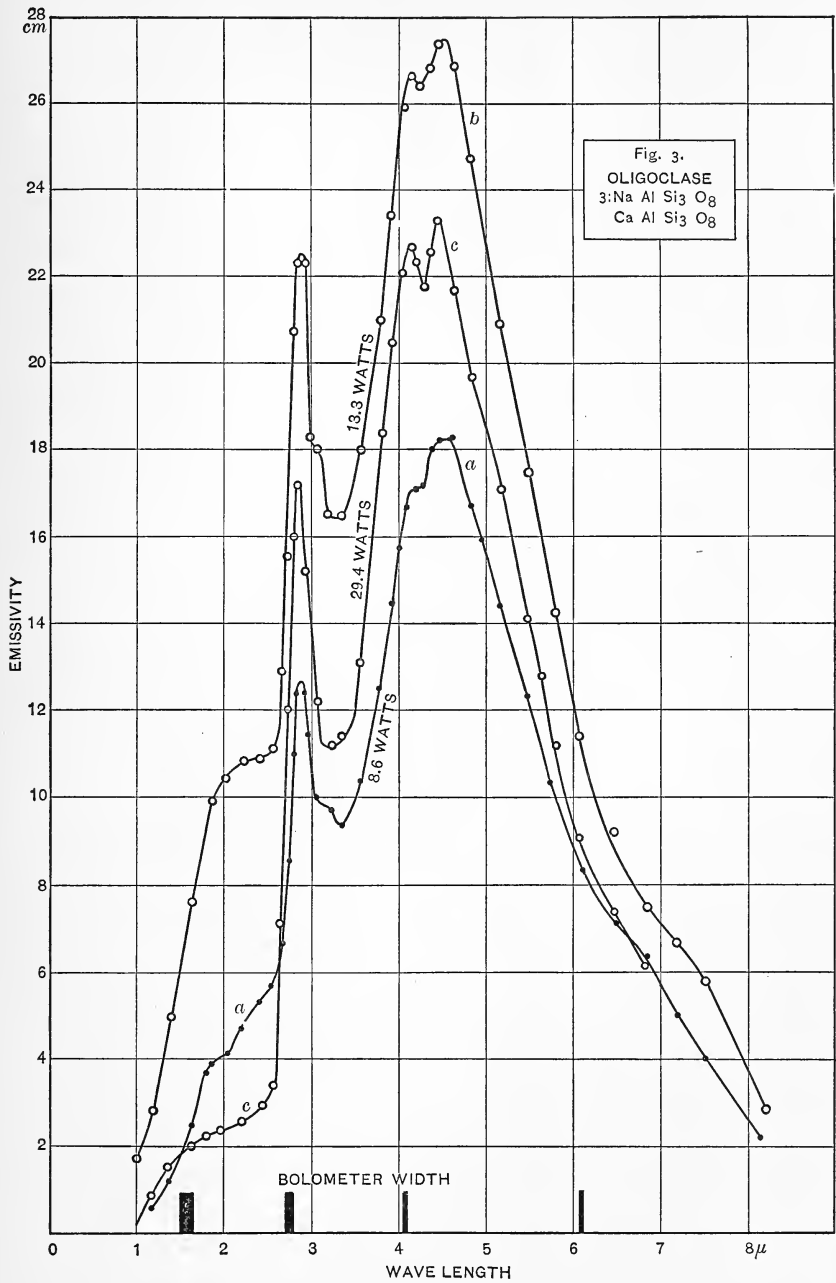
apparent temperature was probably about 1100°. The emission spectrum is unusual in appearance, with a sharp maximum superposed upon it at 2.8μ. There appear to be other ill-defined maxima at 1.7, 2.4, 2.9(?), 3.6, 4.4, and 4.8μ, respectively.

6. *Rutile*.[10]   ($Ti\ O_2$).—[Flat plate, 8 mm long, tapering from 1.5 to 1.8 mm wide and .25 mm thick. Energy supplied, 6 watts. Curve *b*, Fig. 4.] This mineral was heated to a light red color


Fig. 4.
(*a*) Beryl, $Be_3\ Al_3\ (Si\ O_3)_6$
(*b*) Rutile, $Ti\ O_2$
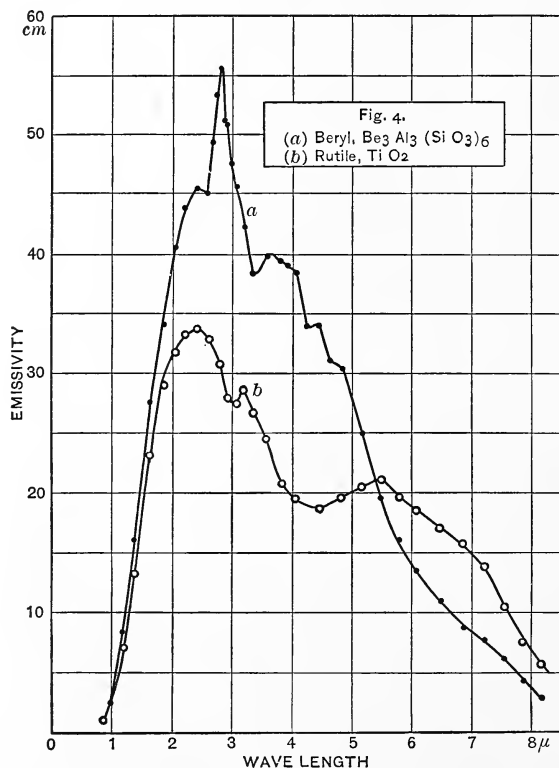
corresponding to a temperature of perhaps 1000°. The terminals were of copper melted to the rutile plate. The emission spectrum shows maxima at 2.4, 3.2, 5.5, and 7.0μ. The transmission spectrum is too low to show these as absorption bands; but the band at 3.1μ is visible in the transmission spectrum of brookite, $Ti\ O_2$. This substance is a good conductor of electricity at this temperature, but a very poor radiator of light rays.

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[10] Transmission curve of this plate given in Carnegie Publication, No. 65, p. 67.

7. *Porcelain* (*Pyrometer Tubing*).—[Hollow rod, 15 × 2 mm; hole, 1 mm. Energy supplied, about 8 watts. Curve *a*, Fig. 5.] The sample of pyrometer tubing examined was heated to a light red color (1400°) to keep it conducting. The energy spectrum is marked for its strong emission, with sharp maxima at 1.8, 2.1, 2.83, 3.7, 4.1, and 4.5μ, with indications of bands beyond 6μ.

8. *Magnesia* (*Pyrometer Tubing*).—[Hollow rod, 12 × 1.5 mm; hole, 1 mm. Energy supplied, about 8 watts. Curve *b*, Fig. 5.]

Fig. 5.
a = Porcelain
b = Magnesia
c = Glass ("Soft Glass")
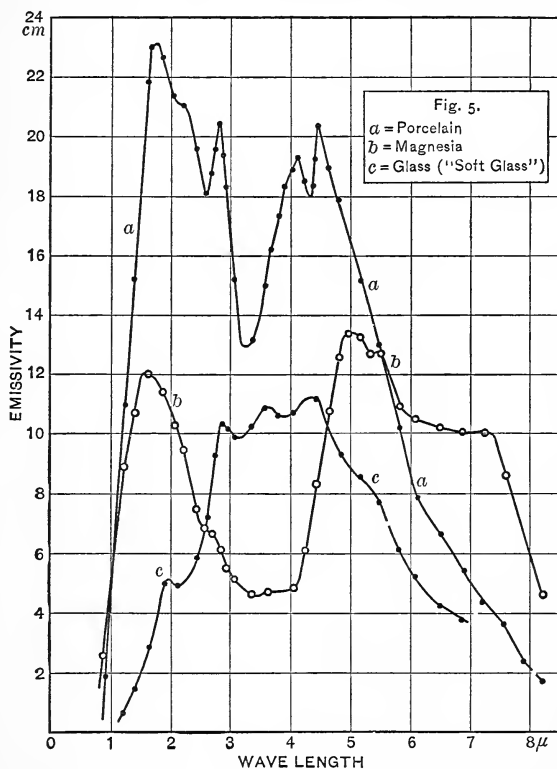
This material is used to insulate thermocouples and conducts only at high temperatures. It is probably a compound of magnesium oxide and silica. The temperature was probably 1200° to 1400°. The emission spectrum is conspicuous for two regions of strong emissivity at 1.6 and 5μ, respectively, with a deep depression at 3.5μ. The emission bands at 1.6, 2.7, 5, 5.5, and 7.1μ are not well resolved, but their presence cannot be doubted.

9. *Glass* [11] (*Soft*).—[Rod, 3 × 2 mm, heated to a dull red color. Curve *c*, Fig. 5.] The substance examined was a piece of ordinary "soft" white glass tubing drawn into a solid rod. There are emission bands at 2, 2.9, 3.6, 4.4, and 5.5μ, respectively.

10. *Glass* (*Cobalt Blue*).—[Rod, 12 × 2 mm. Energy supplied, 0.64 and 1.15 watts. Curves *a* and *b*, Fig. 6.] This rod was heated to a dull red. The emission spectrum is quite different from that of soft glass, but there are no such marked bands as one might expect from a knowledge of the prominent absorption bands

Fig. 6.
a,b = Cobalt glass
c = Apatite
[(Ca F (P O4)3]
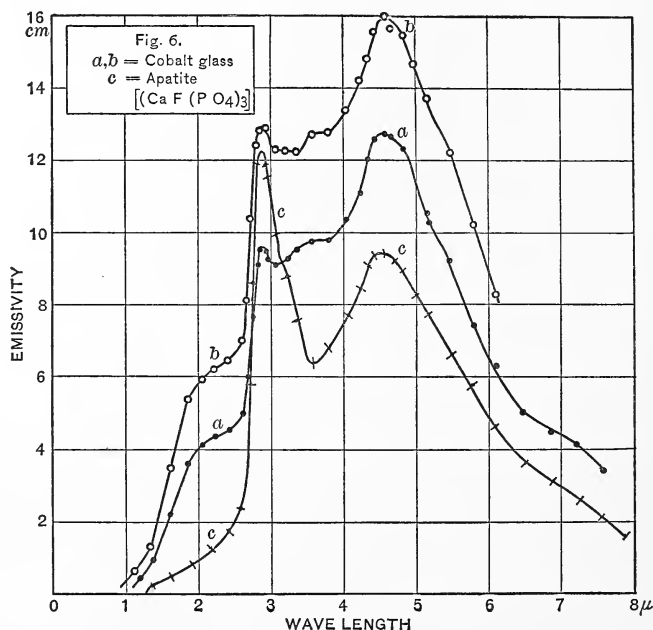
at 1.6 and 2.2μ, which exist in cobalt glass. The silicate band at 2.9μ is prominent. Other bands occur at 2, 3.6, 4.6, and 5.5μ respectively.

11. *Apatite*[12], Ca_5 F $(PO_4)_3$.—[Rod, 12 × 1.5 mm. Energy supplied, 9.3 watts. Curve *c*, Fig. 6.] The emission spectrum shows bands at 2.9 and 4.5μ. The rod was made from a gray, massive specimen, which may have contained silica, whence the band at 2.9μ in both the emission and absorption spectrum.

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[11] Transmission curve. Carnegie Publication, No. 65, p. 64.
[12] Transmission curve. Carnegie Publication, No. 65, p. 58.

However, many oxides known to be free from silica have a strong emission band in this region, from which it would appear that this band is characteristic of the oxide.

12. *Topaz* [(*Al F*)₂ *Si O₄*].—[Rod, 13 mm long, 2 to 2.5 mm diameter. Curves *a* and *b*, Fig. 7]. This rod was made from the massive transparent mineral. The curve is conspicuous for the sharpness of the emission bands which occur at 1.4, 2.85, 4.1, 4.5, and 7.5μ, respectively.

III. EMISSION SPECTRA OF SOLIDS ON NERNST "HEATER-TUBE."

In examining the radiation from solids placed upon a heater it is possible to have some of the radiation from the latter transmitted through the former. If the substance to be examined is in the form of a fine powder and the layer is from 1 to 1.5 mm thick there is but little chance for the radiation to be transmitted from the heater. This fact enables one to study the selective emission of solids which can not easily be formed into solid rods, and is applied in examining the following list of substances:

1. *Zirconium Oxide* (*Zr O₂*).
   Magnesium Oxide (*Mg O*).

[Layer of oxide 0.8 to 1.5 mm thick, on Nernst heater tube from which the clay covering had been removed. Fig. 8, curve *a* is for zirconia.] The zirconium oxide was the pure material and was heated to a dull red, being at a somewhat lower temperature than the rod heated electrically. The emission spectrum is conspicuous for its two sharp emission bands at 2.83 and 4.3μ, respectively. Smaller maxima appear at 2, 2.4, and 5.4μ.

The magnesium oxide spectrum shows two wide bands, at 3 and 5.3μ, respectively, with a smaller band at 2.1 and a deep depression at 3.5μ.

2. *Cerium Oxide* (*Ce₂ O₃*).
   Thorium Oxide (*Th O₂*).
   Uranium Oxide (*U₂ O₃*).

The Cerium oxide curve (*c*, Fig. 7) shows a strong emission at 2 to 3μ, as was shown by Rubens, with possible bands at 4.4 and 7.5μ. It was shown by Rubens[4] that beyond 7.5μ the emissivity approaches that of a complete radiator. For the Welsbach gas mantle which is composed of 99% $Th O_2 + 1\%$ Ce_2O_3 Rubens

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Fig. 7.
Topaz, (Al F)$_2$ Si O$_4$
Cerium Oxide (Ce$_2$ O$_3$)
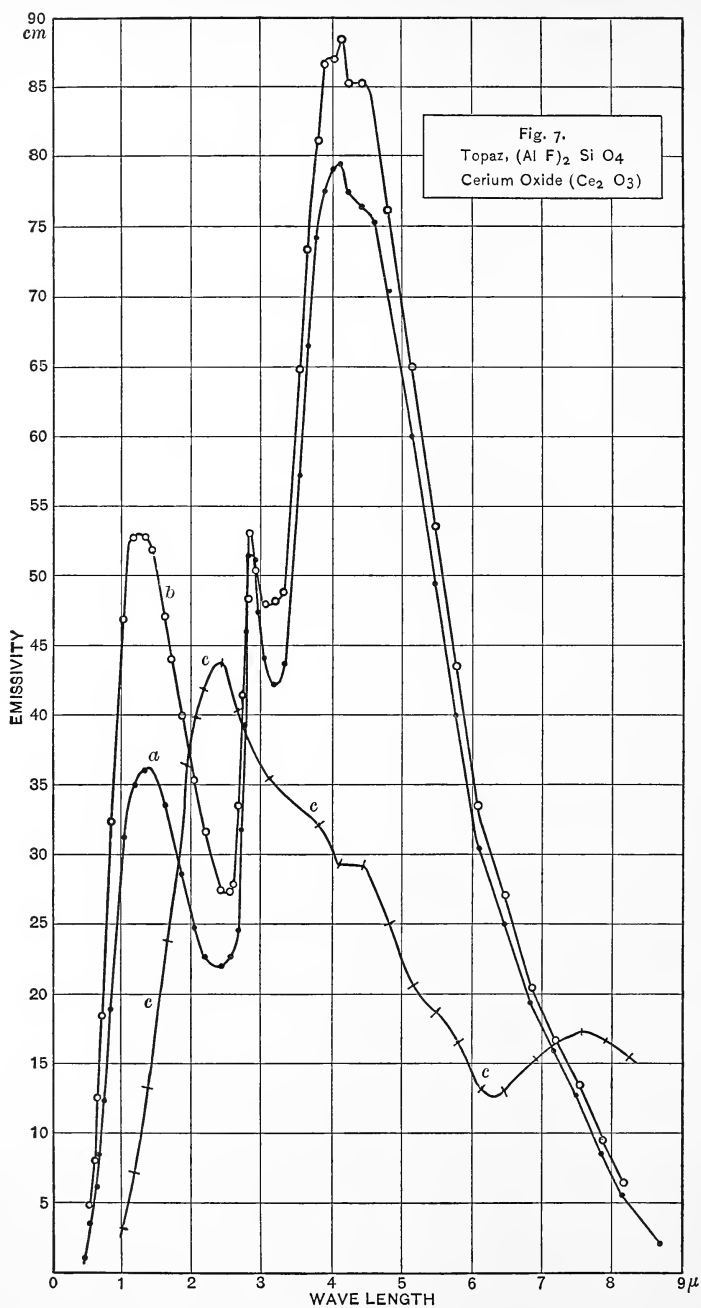
found the radiation curve to be flat and suppressed, similar to curve b, Fig. 8. A rod 1 mm diameter, made of 99% Th O_2 + 1% Ce_2O_3 and heated white hot, electrically, gives an entirely different spectrum from the gas mantle, curve d, Fig. 8. It is probable that this is due to the thickness of the radiating layer.

The Thorium oxide curve (b, Fig. 8) shows no marked emission bands, and the whole spectrum to 7μ is suppressed. Beyond this

Fig. 8.
a = Zirconium Oxide (Zr O_2)
b = Thorium Oxide (Th O_2)
c = Beryllium Oxide (Be O)
d = Thorium + Cerium
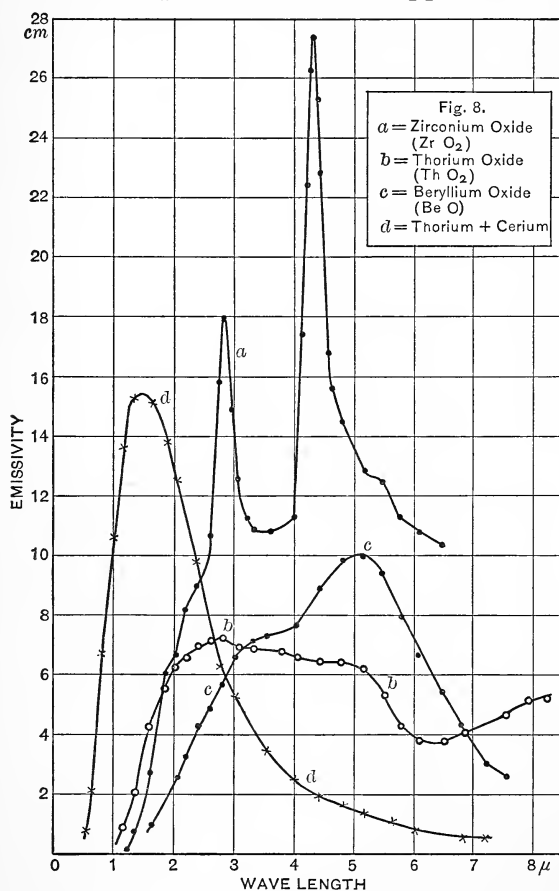
point the emissivity is high, corresponding closely to that of a complete radiator, as was shown by Rubens, using a gas mantle of this material.

The Uranium oxide is a greenish-brown powder which gives a smooth, continuous spectrum with hazy maxima at 2.8μ and 3.4μ, respectively.

3. *Beryllium Oxide (BeO).*—[Curve *c*, Fig. 8.] The Beryllium oxide emission spectrum is smooth, with two wide maxima at 3.5 and 5μ, respectively. The temperature was such that a faint red showed through the interstices of the layer of white oxide.

4. *Yttrium Oxide (Y$_2$O$_3$).*—[Curve *a*, Fig. 9.] The surface color was a deep red, corresponding to a temperature of 900° to 1000°. The curve shows emission maxima at 2, 2.76, 3, 3.6, 4.6, and 6.9μ, respectively, the latter band being unusually sharp.

Fig. 9.
(*a*) Yttrium Oxide (Y$_2$ O$_3$)
(*b*) Erbium Oxide (Er$_2$ O$_3$)
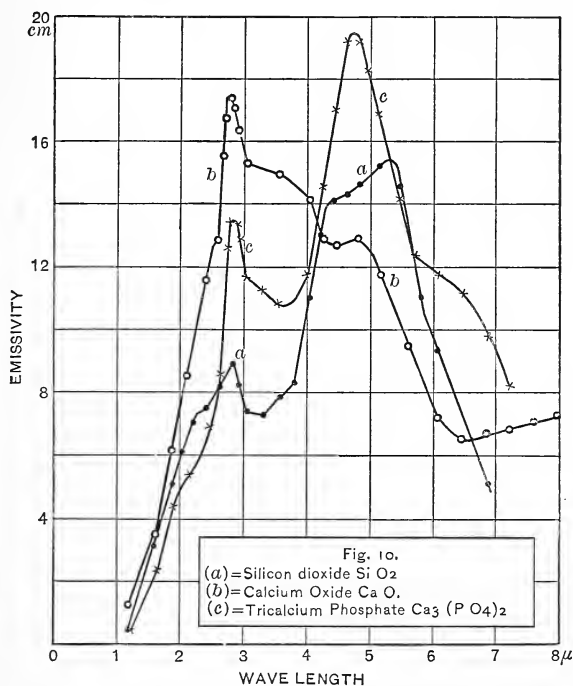(*c*) Neodymium Oxide (Nd$_2$ O$_3$)
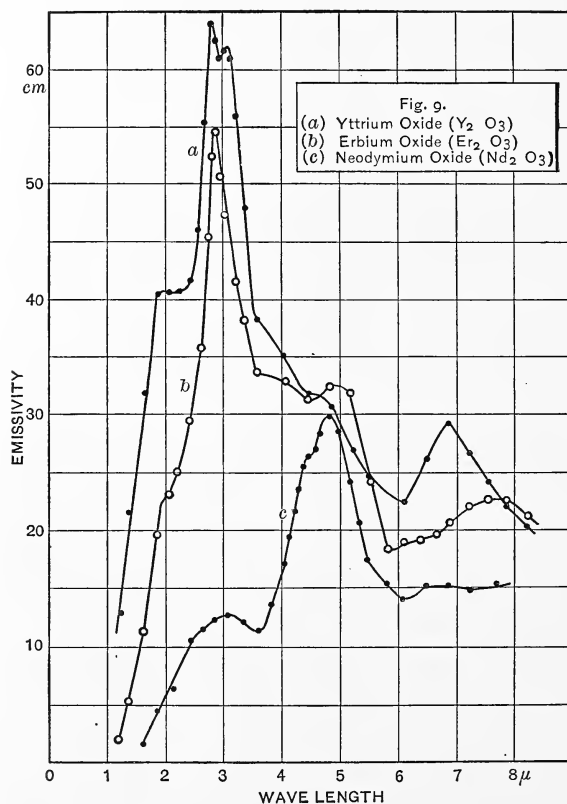
5. *Erbium Oxide (Er$_2$O$_3$).*—Curve *b*, Fig. 9, shows the emission of a layer of the oxide, formed by decomposing a solution of the nitrate on a strip of platinum, heated electrically. There is a sharp emission band at 2.85μ. Other maxima appear at 2, 3.2, 4.1, 5, and 7.5μ. The general outline of the spectrum is similar to that of Yttrium.

6. *Neodymium Oxide (NdO)*.
  Manganous Oxide (MnO).

[Curve *c*, NdO, Fig. 9.] The neodymium oxide was deposited in a thick layer upon a strip of platinum by decomposing a solution of the nitrate. The radiation curve shows maxima at 3, 4.4, and 4.8μ. Beyond 6μ the emissivity is strong and not unlike that of cerium and thorium.

The manganous oxide was of a grayish-brown color. The thickness of the layer upon the "heater tube" was about 1.2 mm.

Fig. 10.
(*a*) = Silicon dioxide Si O_2
(*b*) = Calcium Oxide Ca O.
(*c*) = Tricalcium Phosphate Ca_3 (P $O_4)_2$

The radiating surface was a dull red. The spectral radiation curve is uniformly smooth throughout its whole length, with but a slight depression at 3.2μ, observed in numerous oxides.

7. *Silicon Dioxide (SiO$_2$)*.—[Curve *a*, Fig. 10.] The radiating layer was a fine powder upon a heater tube, heated to a dull red. There are emission bands at 2.2, 2.9, 4.3, and 5.3μ, respectively.

8. *Calcium Oxide (CaO)*.—[Curve *b*, Fig. 10.] The radiating surface was a dull red. The emission curve is conspicuous for its

two sharp maxima at 2.8 and 4.75μ, respectively, and a high emissivity at 8μ, which is similar to cerium and thorium. Smaller bands appear at 2.4, 3.3, and 4μ. The calcium oxide was heated to a bright red before mounting it upon the heater and was apparently free from the carbonate (see Fig. 11). Since there are no emission bands belonging to that substance, it appears that the water used in making the CaO into a paste was entirely expelled. A chemical analysis of the calcium oxide by Dr. H. C. P. Weber gave no weighable amount of silica, which shows that the band at 2.8μ is not due to that oxide.

9. *Tricalcium Phosphate, $Ca_3(PO_4)_2$.*—[Curve *c*, Fig. 10.] The tricalcium phosphate has two marked bands, at 2.85 and 4.75μ, and smaller bands at 2μ and at 6.2μ, respectively.

10. *Cobalt Oxide (Co_2O_3).*
    Chromium Oxide (Cr_2O_3).
    Stannic Acid (SnO_2).

The cobalt oxide curve is smooth throughout, except the depression at 3μ.

Chromium oxide is green in color, and emits a fairly smooth spectrum with a possible maximum at 5μ. The depression at 3.2μ is prominent.

Stannic acid is grayish-white in color, but, unlike many of the white oxides, it emits a continuous spectrum. The depression at 3.2μ is small. The transmission bands in cassiterite, SnO_2, were found to be small.

11. *Zinc Oxide (ZnO).*
    Lead Oxide (PbO).

The zinc oxide became a yellowish-green on heating, resuming its former white on cooling. In spite of this selective emission in the visible spectrum, the distribution of energy in the infra-red is uniform with the usual depression at 3.2μ. Lead oxide, "plumbago," melts at a low temperature. On heating the color changes from orange to deep red. The emission curve is smooth except for a depression at 3.3μ, which is marked, and at 5.5μ there is a possible emission band.

12. *Calcium Sulphate* [13] *($CaSO_4$ + 2 H_2O).*—[Curve *b*, Fig. 11. Temperature about 900°.] The calcium sulphate used was a

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[13] Transmission curve. Carnegie Publication, No. 65, p. 18.

thick smooth layer of "plaster of Paris," which dehydrated, in part at least, at the red heat used. The emission bands at 2, 3.2, 4.65, and 6.3μ coincide in intensity and position with the absorption bands found in previous work. The band at 4.65μ is shifted from its position at 4.55μ in anhydrite, $CaSO_4$, but coincides with the partially dehydrated selenite, $CaSO_4 + 2 H_2O$, given in Vol. 2, p. 461, Fig. 3 of this Bulletin.

Fig. 11.

(*a*) Calcite Ca C O_3
(*b*) Calcium Sulphate Ca S O_4
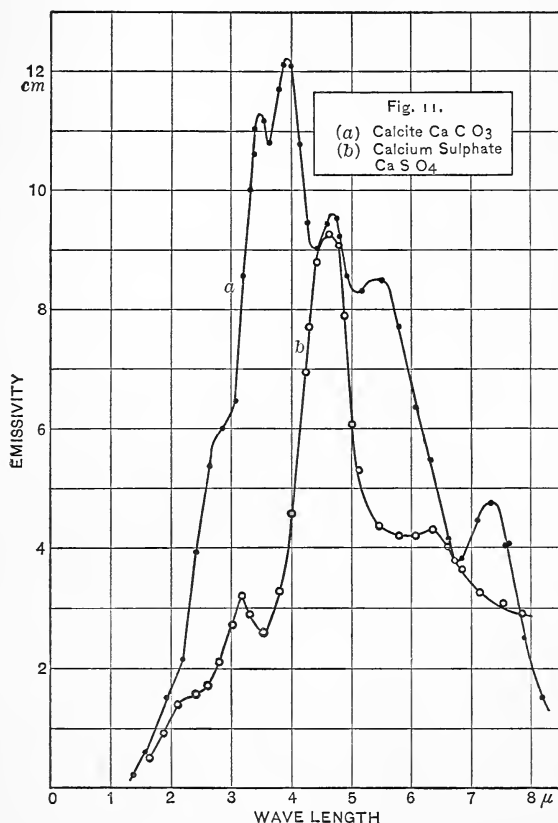
13. *Calcite* [14] $(CaCO_3)$.—[Curve *a*, Fig. 11.] The sample examined was a layer of finely ground white marble. The color corresponded to a temperature of about 900° C. The emission curve is of interest on account of the two types of emission it contains. In the region of 6.7μ calcite has a band of strong selective reflection. In this region of the spectrum the emissivity is pro-

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[14] Transmission curve. Carnegie Publication, No. 65, p. 70.

portional to the reflecting power, thus placing it in the class with metals.   Here the emission is actually suppressed, and we have an emission minimum instead of a maximum.   In the remaining part of the spectrum the emission is proportional to the absorption.   The emission bands at 2, 2.7, 3.5, 3.9, 4.7, and 5.5μ coincide with the absorption bands previously observed.   The apparent maximum at 7.3μ is due to the suppression of the radiation at 6.8μ, as previously described.   This fact can, of course, only be determined from a knowledge of the reflective power of the substance under examination.   The maximum reflection, and the minimum emission do not coincide on account of the high reflecting power on the side toward the long wave-lengths, which suppresses the emission curve, thus shifting the maximum farther into the infra-red.   The only other example is that found by Rosenthal for quartz.[15]

IV. RELATION BETWEEN EMISSIVITY AND ENERGY CONSUMPTION.

The object in examining the isochromatic radiation curves of the solids considered in this paper is to determine whether or not the sharp emission bands, e. g., those in oligoclase, behave like spectral lines or like wide bands which include a considerable portion of the spectrum.

Other phenomena such as the interpretation given to the intersection of the isochromatics are secondary.   If the observed bands behave like emission lines of a gas, then, as previously shown,[16] the emission must be proportional to the energy supplied.   The fact that the maximum does not shift with rise in temperature is strong evidence of the spectral purity of the emission bands, e. g., at 2.9 μ, hence a direct proportionability of emission and energy consumption.   If they are impure spectral lines, then the emissivity can not be proportional to the energy consumption, because the maximum of intensity must shift, due to the difference in the rate of increase in intensity of the different parts of the band, which is caused by the damping action of the different frequencies of the vibrating particles.   Heretofore the spectral partition of

[15] Rosenthal.   Ann. der Phys. (3) 68, p. 791; 1899.

[16] Investigations of Infra-red Spectra, Part II.   Publication No. 35 of Carnegie Institution of Washington, 1905.

radiant energy in terms of energy consumption has not been dis-
cussed, and it is therefore necessary to examine the isochromatic
radiation of a substance of which the radiation laws are known.
The criterion for judging whether the sharp emission bands are
similar to the emission lines of a gas, or similar to the complex
and highly damped emission of a solid, e. g., platinum, is based
upon the behavior of the isochromatic radiation curves, which are
straight lines for a gas, but which are unknown for platinum and
hence must first be determined in the present investigation.

First of all it is well to consider some of the conceptions of the
nature of the mechanism by which the thermal energy within the
radiator is transformed into radiant energy.

According to Stark,[17] and to others, the continuous spectrum is
due to collision of the free electrons with the molecules or with
the positive ions, while the emission bands are due to the internal
vibration of the positive ion ("atomion"). The transformation
of the thermal energy in the positive ion into radiant energy pro-
duces a discontinuous spectrum which follows Kirchhoff's law.
The change of the thermal energy of the free electrons into radiant
energy produces a continuous spectrum.[18]

A complete radiator emits energy, however small the amount,
of all wave lengths, whatever its temperature may be above the
absolute zero.[19] The permanent conductivity in metals indicates a
permanent ionization, and it must therefore behave like the com-
plete radiator in its emission. The isochromatic energy curves
must therefore all begin at the origin of the energy axis; and, as
will be shown presently, they may have a double curvature. On
the other hand, it is a well-known property of spectral lines that
the energy required for excitation is different for different lines,
being independent of the wave length. It is beyond the scope
of the present paper to consider the question whether or not, for
an infinitesimal rise in temperature above the absolute zero, any
spectral lines will be emitted, for if, as is generally supposed, there
is no damping, the emissivity must be proportional to the energy

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[17] Stark.   Ann. der Phys., (4) 14, p. 506, 1904.   A summary of these theories may
be found in Carnegie Publication No. 35, p. 325.

[18] Stark.   Phys. Zs., 8, p. 918, 1907.

[19] Drude's Lehrbuch der Optik., p. 325.

supplied throughout the whole range of temperatures. It seems quite well established that spectral lines are not emitted before the temperature of the gas has been raised a finite amount above the absolute zero.[20] Therefore, the smaller the radiation coefficient the higher must the temperature be raised in order to cause emission.[21]

From these considerations it appears that the emission of a spectral line is proportional to the energy consumption, and since a finite amount of energy must be supplied to excite them, that the isochromatic energy curve must intersect the energy axis at some distance from its origin.

The substances just described must have one or both of two kinds of spectral energy distribution, due (1) to the general absorption which is present to some extent, however small, and which gives rise to a continuous spectrum, and (2) to bands of selective absorption which give rise to emission bands. It is therefore of interest to examine their isochromatic radiation curves by plotting emissivity against energy consumption instead of against temperatures, as has been done heretofore. In plotting isochromatics of emissivity against temperature it is unnecessary to correct for slit width, but if we wish to compare different isochromatics of emissivity plotted against energy consumption, then it is necessary to reduce all the observations to the same bolometer sensibility, and also to correct for slit width in order to reduce the emissivities to a common origin. If the wave lengths of two isochromatics are close together, as for example $\lambda = 1.804\mu$ and $\lambda = 1.968\mu$ in Fig. 12, the error introduced in the determination of the energy consumption (without correcting for slit-width) at the point of intersection of two isochromatics is less than 3 per cent and could be made still less by selecting two wave-lengths which are closer together.

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[20] B. Davis. Phys. Rev., **20**, p 145, 1905, shows that the energy necessary to ionize a molecule is of the order of 5×10^{-12} erg.

See also papers by Townsend, Phil. Mag., (6) **1**, 209, 1901; and by Nutting. Astrophys. Jour., **21**, 404, 1905.

[21] Stark. Phys. Zs., **8**, p 919, 1907, computes that in order to bring the D-lines to emission as the result of collision of moving sodium ions they must have a kinetic energy larger than 3.2×10^{-10} erg., while the collision of the negative electron would cause the D-lines to be emitted with a kinetic energy of less than 10^{-11} erg.

It is of course impossible to determine the true energy con-
sumption in short filaments, on account of the losses by conduc-
tion from the ends and by convection, so that the true energy
supplied, especially at high temperatures, is probably higher than
here recorded.   But this can not affect the conclusions to be
drawn from the isochromatics, for the error in the observed energy
consumption must affect *all* the isochromatics, in the same man-
ner, while in the results to be mentioned presently the isochro-
matics for the *different wave lengths are affected differently*, which
seems to be conclusive evidence that the cause is not due to lack
of knowledge of the energy supplied (which would produce a still
greater curvature of the isochromatics toward the axis of energy),
but is due to a variation in emissivity with change in energy con-
sumption.

The present results show that, for solids having a fairly smooth,
continuous emission spectrum, as the maximum emission, E_{max},
shifts toward the short wave-lengths, the isochromatics close to,
and of shorter wave-length than, the λ_{max}, E_{max}, suddenly bend
upwards (away from the energy axis), and after the E_{max} passes
over these wave-lengths, so that the isochromatics lie on the long
wave-length side of the λ_{max}, E_{max}, then their curvature changes
in the opposite direction.   In other words, there is a point of
inflection when the isochromatic wave-length is identical with the
λ_{max}.   The interpretation of this is, of course, the well-known
property of spectral emission of a complete radiator and of metals
in which the emissivity in the short wave lengths increases more
rapidly with rise in temperature than in the long wave lengths,
whence the shift of the maximum of emission.

1. *Isochromatics of platinum.*—The aforesaid double curvature is
well illustrated in Fig. 12, in the isochromatic radiation curve of
platinum at 2.75 μ.   The isochromatic at 3.578 μ has but a single
(downward) curvature, since the temperatures were all higher
than that required to cause the λ_{max} to be equal to or greater than
3.578 μ.

The platinum strip was 50 × 1.5 × 0.02 mm in an exhausted glass
bulb with a fluorite window; hence convection losses are small.
In this figure the graphs of wave lengths $\lambda = 1.804 \mu$ and $\lambda = 1.968 \mu$,
intersect at about 3.0 watts, showing that the maximum of the

energy curve lies between (but not halfway) these two wave-lengths, the temperature being about 1100°C. Using these two wave lengths the λ_{max}, for this energy input, can be calculated from the equation given by Paschen.

In Fig. 12 the slit-width correction has not been applied to the isochromatics, except for $\lambda = 1.804 \ \mu$ and $\lambda = 1.968 \ \mu$ (short upper-most graphs, Fig. 12), which shows a small correction to the energy input. The other isochromatics are not comparable on account of different bolometer sensibilities.


Fig. 12.
ISOCHROMATIC RADIATION CURVES OF PLATINUM
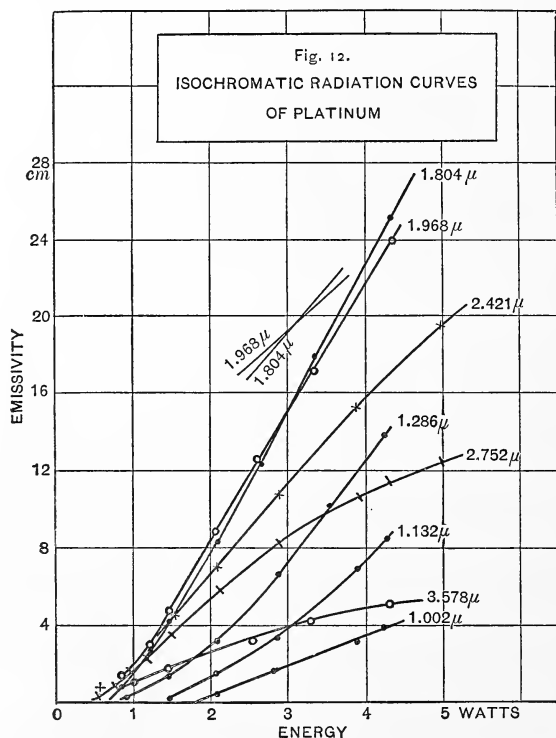
2. *Isochromatics of Nernst glower.*—In a preceding paper[22] on the selective emission of the Nernst glower the writer concluded that because the spectrum was discontinuous at low temperatures it must behave likewise at high temperatures (provided a large enough dispersion could be obtained) and hence, since the emission of spectral lines is proportional to the energy, that the appli-

[22] See results on Nernst glower; this Bulletin, **4**, p. 546, 1908.

cation of isochromatics of emissivity plotted against temperature (assuming Wien's equation), as made by other observers, must give too high values for the temperature of the glower. The isochromatics obtained by the present method indicate that the Nernst radiation behaves somewhat like that of a metal and of a complete radiator (emissivity not quite proportional) to the energy input, but more nearly so than for platinum, so that the former conclusion must be somewhat modified to admit this data. However, the position of the λ_{max} and E_{max} does not admit the highest temperatures given by others.

Furthermore, if we follow the usual assumptions (see Kayser, Spectroscopic, Vol. II, pp. 59, 245, and 331) and consider the separate lines as a part of an energy curve, obtained by drawing the envelope through the highest points of the separate emission bands, then the maximum of the envelope must shift toward the short wave lengths with increase in energy consumption, and the slant of the isochromatics must be similar to those of platinum, Fig. 12. It is difficult to conceive how this is possible with discrete spectral lines which require the application of a certain amount of energy to excite them.

The change of the emission curves of the Nernst glower from a discontinuous into a continuous spectrum has been noticed in a previous paper. They illustrate this envelope type of energy curve just mentioned. But it seems more probable that this is due to the rapid growth of the general emission of the intervening frequencies which, with a doubtful broadening of the emission band (see figs. 1 and 2), obliterates the selective emission at high temperatures. In Fig. 13 are given a series of isochromatics for a 110-volt Nernst glower 1.4 cm long and 1.4 mm in diameter. The current was supplied from a 2000-volt 600-watt transformer on a 110-volt circuit. The supply of energy was regulated by means of resistances in the primary. The voltage was obtained with a multiple-cell electrostatic voltmeter. The curves (not corrected for slit-width and bolometer sensibility) for the most intense part of the spectrum pass through a slight double curvature, thus giving them the general outline of that of platinum. The normal burning is 80 watts and above that point the isochromatics appear to show a slight increase in curvature. The inter-

Fig. 13.

ISOCHROMATIC RADIATION CURVES
OF NERNST GLOWER.
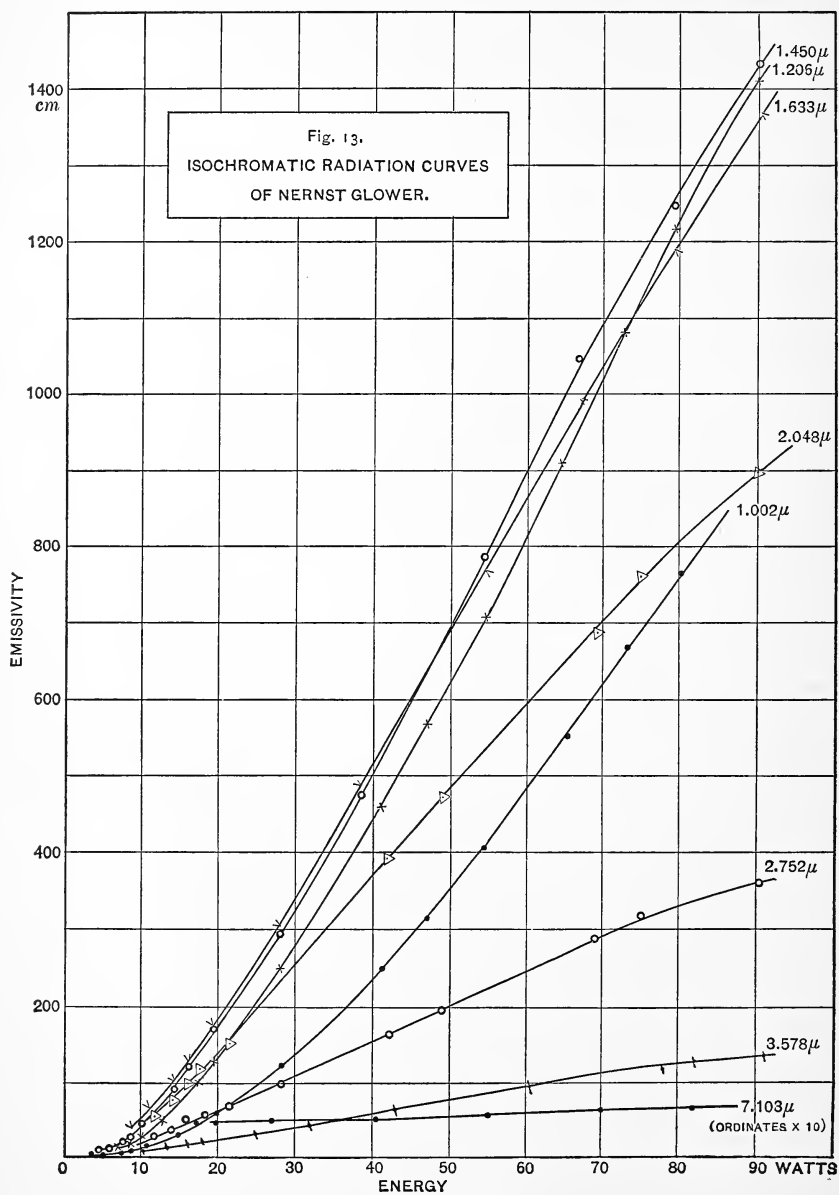
section of the graphs for wave lengths $\lambda = 1.206$ μ and $\lambda = 1.633$ μ at 73 watts (somewhat greater if slit-width correction is applied) shows that the maximum of the spectral energy curve, for this power consumption, lies between these two points, as previously observed.[22] This method of locating the maximum eliminates the correction for slit width, and is an independent proof of the previous observations that the maximum of the energy curve for normal burning (80 watts) does not lie at such short wave lengths as was observed by previous investigators. This of course is on the assumption that the glowers were of the same material (see curve *b*, Fig. 8, for other substances), the base of which is zirconium oxide with a small percentage of cerium, thorium, or yttrium oxide.

3. *Isochromatics of oligoclase.*—In No. 35, p. 318, of Carnegie Publications, it was shown that in the case of vacuum tube radiation the intensity of the emission lines is proportional to the energy consumption. The graphs there obtained, showing the relation between current and the emissivity of a spectral emission line, are curved due to the fact that Ohm's law does not hold for the vacuum tube discharge. For the present examination, instruments were available to measure the energy consumption when the graph ought to be a straight line, provided the partition of the energy emitted is in discrete lines. As a typical selectively radiating solid, oligoclase was chosen on account of its sharp emission bands, and also on account of its homogeneity. A rod 2.5 cm long and 2.1 mm diameter was prepared in an oxy-hydrogen flame. The spectrometer slit was reduced to 5 mm in length, which permitted the entrance of radiation from only about 5 mm of the central part of the rod, which was a perfectly clear glass, free from air bubbles. At the highest temperatures this central part showed a peculiar faint white "luminescence" similar to the intense white seen in quartz when heated in the oxy-hydrogen flame. The rod was thickened at the ends, which seemed to prevent internal reflection of the radiation from the platinum terminals. The ends of the 0.3 mm platinum terminals within the glass rod were red hot. The rod was viscous at the highest energy input, 29.4 watts, indicating a temperature of at least 1100° to

1200° (melting point about 1300° C); but no light was emitted other than the hazy white glow already mentioned, which is in marked contrast with the radiation from the platinum electrodes. A similar example is given in Wood's Optics, p. 457, where it is stated that sodium sulphate, in a loop of platinum wire, heated in a blast lamp, emits but little light, although the wire glows vividly.

In Fig. 14 are given the isochromatic emission curves of oligoclase at wave-lengths 2.048, 2.905, 4.445, and 6.082 μ respectively, for different values of power consumption. The graphs are for

Fig. 14.

ISOCHROMATIC RADIATION
OF OLIGOCLASE
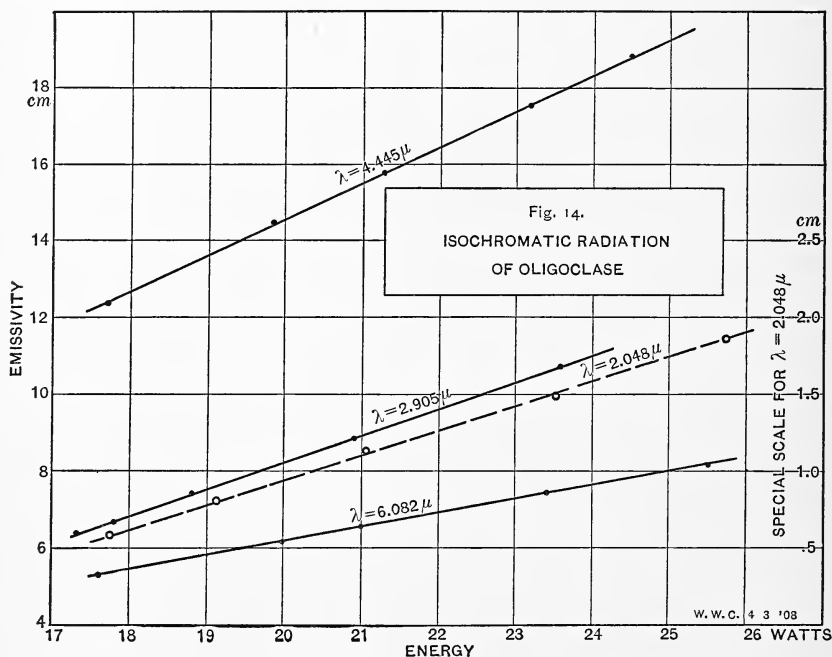
the same rod, under the same conditions of galvanometer sensibility and distance of the radiator from the slit and are corrected for slit width. The complete isothermal radiation curve on 29.4 watts is given in Fig. 3, curve *c*, the scale of ordinates being of course different from those of curves *a* and *b*. Two additional series of observations on different days, and using different adjustments, were made at wave length 2.905 μ. Only one of these graphs was parallel with the one given in Fig. 14, showing that there is a variation in the slant of the isochromatic curve under different con-

ditions due, no doubt, to a variation in the spectrometer setting, to a variation in the homogeneity of the rod, to internal reflection of radiation from the platinum terminals, etc.   It will be noticed that, throughout the range investigated, the change in emissivity of all the lines is proportional to the energy supplied, just as is true of gases.   It is possible that for some wave-lengths the thickness of the radiator was not sufficient to emit a saturated radiation, and this may explain why the emissivity at 2.048 μ apparently does not follow the same law (its slant should be steeper) as do the other emission bands.   In order to have displacement of the maximum of emission, just as is known for solids emitting continuous spectra, it is necessary that the intensity of the emission at the short wave lengths increase more rapidly than it does in the long wave lengths.   The $\lambda = 2.048 \mu$ isochromatic slants only a little less from the normal than does $\lambda = 6.082 \mu$.   In this region of the spectrum there is a weak general absorption while the other wave-lengths are the maxima of selective emission (absorption) bands, and it is possible that what corresponds to the emissivity constant of a complete radiator is different for the two kinds of radiation found in this substance corresponding to what is commonly called "general" and "selective" absorption.   It is possible that the isochromatic at 2.048 μ undergoes a sudden change, curving sharply upward, at a higher temperature.   The same is true of the platinum isochromatic at 1 μ.   In fact, it appears that the emissivity at 2.048 μ must suddenly change in intensity, unless oligoclase is entirely different from the other substances examined; for, like the others, in the oxy-hydrogen flame it emits an intense white light, although, as shown in curve c, Fig. 3, the emissivity at 2 μ is still weak when the temperature is close to the melting point.

In oligoclase it is not possible to locate so definitely, if at all, the position of the maximum of the envelope by the intersection of the isochromatics; for the lines show no tendency to curve, as in platinum, although at closely the same temperature.   By the extrapolation of the 2.9 μ and the 4.4 μ isochromatics, the intersection is found to be at about 8.5 watts.   The maximum emission would then lie at about 3.5 μ, which is the position of the maximum for a complete radiator at 850° Abs. (580° C).   On 29.4 watts,

when the oligoclase was already viscous, indicating a temperature of 1100° to 1200° (melting point 1300°), the maximum emission should be found at a much smaller wave length than 3.5 μ; the emission curve is, however, but little different in outline from those obtained at lower temperatures, Fig. 3, with no indication of a shifting of the energy distribution. It would therefore appear that it is not permissible to consider the envelope, drawn through the emission maxima, as a criterion for judging the temperature of a substance like oligoclase. On the whole, it appears that the general emission, as distinguished from the bands of selective emission, is less intense in oligoclase than in most of the other silicates studied.

V. SUMMARY.

In general, the results on the oxides furnish an excellent illustration of the shifting of the maximum of intensity of emission toward the short wave lengths with rise in temperature, just as is known for metals, which emit continuous spectra. In this respect the various emission curves of zirconium oxide are particularly conspicuous. In addition to what may be termed general emission, in which the maximum shifts with rise in temperature, the curves of zirconium oxide are unique in having a sharp band of selective emission which does not shift nor broaden with rise in temperature.

The results are not unlike those obtained by Anderson[23] for erbium oxide, in the visible spectrum. He found that the emission spectrum was not continuous, but consisted of bright bands superposed upon a continuous faint background. With rise in temperature the bands became more hazy in outline, and at very high temperatures the spectrum became continuous. If, according to Stark's theory, the continuous spectrum is due to the presence of a large number of free electrons, this is to be expected. At low temperatures the electrical conductivity is small, and the emissivity is confined to particular bands caused by certain groups of electrons. With rise in temperature more electrons, extending over a wider range of wave-lengths, are excited to activity and the separate emission bands become merged into a continuous spec-

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[23] Anderson.   Astrophys. Jour., **26**, p. 73; 1907.

trum. This is not always true, however, in the present work. For example, the sharp emission band of zirconium oxide at 4.3μ seems to retain the same intensity, superposed upon a continuous background of increasing intensity, irrespective of the temperature. In fact many of the emission bands are as sharp as those found in gases.

Many of these oxides have an emission band in common in the region of 2.85μ, from which it would appear that this band may be due to the oxygen atom which is in common with all of them. Furthermore, the emission spectra, when smooth, generally show a depression at 3.2μ, for which no satisfactory explanation has been found. There are no atmospheric absorption bands in this region, and fluorite is not known to have absorption bands at this point. The emission spectrum of platinum, carefully examined at the same time, showed no depression. The emission curve of the bare "heater tube" which consists of a porcelain tube wound with fine platinum wire, likewise gave a smooth emission curve similar to that of the platinum strip. The present data indicate that the depression is a characteristic of the oxides. In other words, the oxides have a large (sometimes small) characteristic emission band at 2.8 to 3μ and a second group of bands at 4.5 to 5μ. If this be true, then it will be necessary to assign the cause of the selective emission to the element common to all the oxides, viz., to oxygen. It is well known that groups of atoms have characteristic bands, but, heretofore, no data has been at hand which in any way indicated the possibility of the characteristic bands being due to a particular atom in the group. The tentative conclusion that these emission bands in the oxide are due to oxygen atoms should perhaps be expected. The oxides are the most important and the most stable of all the important groups of chemical compounds; and the spectra belonging to a particular group are similar. But few substances are inert to the action of oxygen. The spectrum of oxygen[24] shows absorption bands at 3.2 and 4.75μ. The emission spectra of CO and CO_2 show bands in the region of 2.7 and 4.75μ. Oxygen in a vacuum tube showed an emission band at 4.75μ, which at that time was ascribed to CO

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[24] Carnegie Publication, No. 35, pp. 49 and 313.

or CO_2 formed by the electrical discharge. In view of the fact that, with rise in temperature, the CO_2 emission band shifts towards that of CO at 4.6μ, and that eventually all three gases, CO_2, CO, O, when radiating by electrical excitation in a vacuum tube, have their important emission band in common at 4.75μ, it does not seem unreasonable to assume that the latter maximum is due to the oxygen atom, set free during the time intervening between dissociation and recombination brought about by the electrical discharge.

In a broad sense the intensity and sharpness of the emission bands are a function of the electrical conductivity. The best insulators, e. g., the refractory silicates, the oxides of zirconium, erbium, etc., have the sharpest emission bands, while the better electrical conductors such as the oxides of cerium, iron, zinc, etc., have a high emissivity but no sharp emission bands throughout the infra-red. The molecular weight of the base seems to affect the sharpness of the bands to as great an extent as does the electrical conductivity. These results, if true, are to be expected from our knowledge of the emission, absorption, and reflection of electrical conductors and insulators.[25]

If the oxides behave like metals, in which the reflecting power is proportional to the electrical conductivity then from one line of theoretical consideration one would expect to find an increase in the reflective power,[26] with rise in temperature, and the accom-

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[25] Kirchhoff's Law says that for a given temperature, T, and wave length, λ, the emissivity E, the absorptivity, A, and the reflectivity, R, of a substance is related to the emissivity, e, of a black body, by the equation $E = Ae = (1-R)$ e, since $A = 1-R$.

For "transparent media," "electrical insulators" the reflectivity, R, the index of refraction n, and the extinction coefficient, k, are related as follows:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

For electrical conductors, metals, the reflectivity is related to the electrical conductivity by the relation, $100 - R = \frac{36.5\sqrt{w}}{\sqrt{\lambda}}$ where w is the specific resistance.

This subject has been thoroughly treated by Aschkinass, Ann. der Phys., (4) **17,** p. 960; 1905.

[26] Rubens. Ann. der Physik, (4) **20,** p. 593, found that the Welsbach mantle may or may not *decrease* in reflective power with rise in temperature, and chemical composition. The reflective power of the oxides is low (5 to 6 per cent) which may account for this disagreement.

panying increase in the electrical conductivity of the oxides. If this be true, then it would seem that the spectral emission ought to become more continuous, as is found in the Nernst glower.

It may be added that the positions of the well-defined maxima of emission are not affected by change in temperature. Whether the emission maxima at 2.85 and 4.75μ are due to the presence of water remains undetermined. If they are due to water, then one would expect to find them in calcium sulphate, $CaSO_4 + 2H_2O$, as well as in calcium oxide (probably some CaOH present); in the sulphate no band was found at 2.9μ where the emission should be the most intense, if due to water. The sulphates[27] have a characteristic band at 4.75μ; but from the present data it is no more satisfactory to assume that the bands at 2.85μ and 4.75μ found in the oxides, are due to the presence of water than to ascribe them to the common constituent, viz., oxygen.

The isochromatics of oligoclase show that the emissivity is proportional to the energy input, thus differing from the other solids investigated, but, in view of the fact that in the oxy-hydroden flame it emits an intense white light, it appears that the emissivity must suddenly undergo a change in the visible spectrum, and perhaps form a more continuous spectrum throughout the infra-red.

WASHINGTON, May 20, 1908.

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[27] This Bulletin, Vol. **2**, p. 469.